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CLAIMS

[Claim(s)]
[Claim 1] The negative electrode for nonaqueous electrolyte cells with which the X-ray reflective peak intensity of the crystal face acquired to the incidence X-ray from [on said front face of a sheet] a normal (200) is 50% or more of the sum of the whole reflective peak intensity obtained from said incidence X-ray, and is characterized by having arranged the coat which has the matter of the rock salt mold crystal structure on the front face of said sheet in the sheet which uses a lithium as an active material.
[Claim 2] The coat which has the matter of the rock salt mold crystal structure is a negative electrode for nonaqueous electrolyte cells according to claim 1 characterized by being the structure which carried out orientation to the sheet front face in 50% or more of the specific crystal face.
[Claim 3] The negative electrode for nonaqueous electrolyte cells according to claim 2 with which the orientation side of the coat which has the matter of the rock salt mold crystal structure is characterized by being the crystal face (100) of said rock salt mold crystal structure.
[Claim 4] the lattice constant a of the coat which has the matter of the rock salt mold crystal structure -- $4.46 < a < 5.45$ it is -- negative electrode for nonaqueous electrolyte cells according to claim 1, 2, or 3 characterized by things.
[Claim 5] the lattice constant a of the coat which has the matter of the rock salt mold crystal structure -- $4.91 < a < 5.01$ it is -- negative electrode for nonaqueous electrolyte cells according to claim 1, 2, or 3 characterized by things.
[Claim 6] A coat is a negative electrode for nonaqueous electrolyte cells according to claim 1, 2, or 3 characterized by having the halogenide of a lithium.
[Claim 7] The halogenide of a lithium is a negative electrode for nonaqueous electrolyte cells according to claim 6 which is LiCl.
[Claim 8] The negative electrode for nonaqueous electrolyte cells according to claim 1, 2, or 3 characterized by having the solid solution of at least one sort chosen from LiCl, LiBr, and LiI, and LiF as a component of a coat.
[Claim 9] The solid solution is a negative electrode for nonaqueous electrolyte cells according to claim 8 characterized by being the solid solution of LiCl and LiF.
[Claim 10] The negative electrode for nonaqueous electrolyte cells according to claim 7 is the manufacture approach of the negative electrode for nonaqueous electrolyte cells characterized by producing by dipping the sheet which uses a lithium as an active material in the solution containing a chlorine molecule or a chlorine ion.
[Claim 11] The solution containing a chlorine molecule or a chlorine ion is the manufacture approach of the negative electrode for nonaqueous electrolyte cells according to claim 10 characterized by producing by adding the organic solvent which blew chlorine gas, or blowing chlorine gas into the solution containing an organic solvent.
[Claim 12] An organic solvent is the manufacture approach of the negative electrode for nonaqueous electrolyte cells according to claim 11 which is dimethoxyethane.

[Claim 13] The negative electrode for nonaqueous electrolyte cells according to claim 8 or 9 is the manufacture approach of the negative electrode for nonaqueous electrolyte cells characterized by producing by dipping in the electrolytic solution containing at least one sort chosen from (a chlorine molecule, a chlorine ion, a bromine molecule, bromine ion, an iodine molecule, and iodine ion) in the sheet which uses a lithium as an active material, and at least one sort chosen from (a fluorine molecule and fluorine ion).
[Claim 14] The negative electrode for nonaqueous electrolyte cells according to claim 9 is the manufacture approach of the negative electrode for nonaqueous electrolyte cells according to claim 9 characterized by producing by dipping the sheet which uses a lithium as an active material in the electrolytic solution which dissolved LiPF6 and LiClO4.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the negative electrode for nonaqueous electrolyte cells.
[0002]
[Description of the Prior Art] A lithium metal is used for a negative-electrode active material, and since the nonaqueous electrolyte cell which was with the electrolytic solution made to dissolve the salt of LiClO4, LiBF4, LiAsF6, LiPF6, and LiCF3SO3 grade in organic solvents, such as propylene carbonate, gamma-butyrolactone, dimethoxyethane, a tetrahydrofuran, and dioxolane, has a high energy consistency, it is used for the primary cells for small electronic equipment including an electronic clock and a camera today. Moreover, it is expected also as a rechargeable battery of portable equipments, such as a cellular phone, a portable personal computer, and a video movie.
[0003] When this kind of nonaqueous electrolyte cell is used as a primary cell, the chemical reactivity of a lithium metal is high, in order to react with an electrolyte component easily and to form a passive state coat in a negative-electrode front face, a self-discharge reaction is controlled and there are the features that a preservation property is good.
[0004]
[Problem(s) to be Solved by the Invention] However, when this is used as a rechargeable battery, the sludge of lithium metals, such as the shape of arborescence, a needle, and fibril, and the so-called dendrite occur remarkably on a negative-electrode front face during charge. This is because [that the deposit location of the lithium metal ion on a negative-electrode front face localizes for gestalt-heterogeneity] formation of a passive state coat and a reaction front face are crystallographic. Such a dendrite is formed at the time of charge, and in the following discharge process, a dendrite dissolves partially and is cut in pieces. At this time, it becomes impossible to have dissolved all the lithium metals deposited during charge, and there was a problem that charge-and-discharge effectiveness fell remarkably as a result. Moreover, when growing up without cutting a dendrite in pieces, the internal short circuit between a negative electrode and a positive electrode arose, and there was also a problem that a charge-and-discharge cycle life became short.
[0005] This invention solves such a technical problem, controls generating of a dendrite, and aims at offering a reliable nonaqueous electrolyte cell with the cycle life over a long period of time.
[0006]
[Means for Solving the Problem] It is the negative electrode for nonaqueous electrolyte cells which this invention is 50% or more of the sum of the whole reflective peak intensity from which the X-ray reflective peak intensity of the crystal face acquired to the incidence X-ray from [on said front face of a sheet] a normal (200) is obtained from said incidence X-ray in the sheet which uses a lithium as an active material, and is characterized by having arranged the coat which has the matter of the rock salt mold crystal structure on the front face of said sheet.
[0007] As for the coat which has the matter of the rock salt mold crystal structure, at this time, it is effective that 50% or more of the specific crystal face is the structure which carried out orientation to the

sheet front face.

[0008] Furthermore, it is desirable for the orientation side of the coat which has the matter of the rock salt mold crystal structure to be the crystal face (100) of said rock salt mold crystal structure.

[0009] moreover, the lattice constant a of the coat which has the matter of the rock salt mold crystal structure -- 4.46 < -- a< 5.45 it is .

[0010] furthermore, the lattice constant a of the coat which has the matter of the rock salt mold crystal structure -- 4.91 < -- a< 5.01 it is -- things are desirable.

[0011] Moreover, it is desirable for the coat which has the matter of a rock salt mold crystal structure to have the halogenide of a lithium.

[0012] Furthermore, as for the halogenide of a lithium, it is desirable that it is LiCl. Moreover, it is useful to have the solid solution of at least one sort chosen from LiCl, LiBr, and LiI and LiF as a component of a coat.

[0013] As for said solid solution, at this time, it is desirable that it is the solid solution of LiCl and LiF. Moreover, although the negative electrode for nonaqueous electrolyte cells of this invention is produced by dipping the sheet which uses a lithium as an active material in the electrolytic solution containing a chlorine molecule or a chlorine ion, it is made.

[0014] As for the solution containing a chlorine molecule or a chlorine ion, at this time, it is useful to produce by adding the organic solvent which blew chlorine gas, or blowing chlorine gas into the solution containing an organic solvent.

[0015] Furthermore, as for an organic solvent, it is desirable that it is dimethoxyethane. Moreover, the negative electrode for nonaqueous electrolyte cells of this invention is producible by dipping in the electrolytic solution containing at least one sort chosen from (a chlorine molecule, a chlorine ion, a bromine molecule, bromine ion, an iodine molecule, and iodine ion) in the sheet which uses a lithium as an active material, and at least one sort chosen from (a fluorine molecule and fluorine ion).

[0016] Furthermore, it is producible by dipping the sheet which uses a lithium as an active material in the electrolytic solution which dissolved LiPF6 and LiClO4.

[0017]

[Embodiment of the Invention] In order to control dendrite generating of a lithium metal, it is desirable to repeat a deposit uniform in energy and advance of lytic reaction, and to perform them. For that purpose, the homogeneity of the surface reaction in the front face on which the homogeneity of the crystal structure of the lithium metal itself and a reaction occur, and a surface coat is required.

[0018] The negative electrode to which the crystal face in the body-centered cubic lattice crystal structure (100) has the surface coat structure where the surface coat of the rock salt mold crystal structure currently formed with adjustment sufficient to the atomic arrangement of the front face was made to form, as a means for that with the sheet which uses a lithium metal as an active material in a lithium sheet with the uniform structure which is carrying out orientation with the priority to a sheet front face is used for a nonaqueous electrolyte cell.
 [0019] Moreover, in forming LiCl as crystal matter of a rock salt mold, it produces by dipping the lithium sheet in which the crystal face (100) is carrying out orientation with the priority to a sheet front face in the electrolytic solution containing a chlorine molecule or a chlorine ion.

[0020] Furthermore, the value of 4.96 of the superlattice period in the crystal face (100) of a lithium metal is received. In order that the solid solution of at least one sort and LiF may form the surface coat which is the principal component of a surface coat among LiCl, LiBr, and LiI as a surface coat of the rock salt mold crystal matter with a comparable lattice constant (100) The lithium sheet in which the crystal face is carrying out orientation with the priority to a sheet front face The negative electrode for nonaqueous electrolyte cells is produced by dipping in the electrolytic solution which contains at least one sort, a fluorine molecule, or fluorine ion among a chlorine molecule or a chlorine ion, a bromine molecule or bromine ion, an iodine molecule, or iodine ion.

[0021] Hereafter, the gestalt of the operation is concretely indicated about the negative electrode for nonaqueous electrolyte cells of this invention.

[0022] When X-ray analysis was performed about the lithium foil immediately after acquisition using

CuK alpha rays, each peak equivalent to the crystal structure of the body-centered cubic lattice mold corresponding to Li metal (number 150401) of a JCPDS card had appeared. There are no other peaks and they showed the metal lithium of a body-centered cubic lattice mold altogether.

[0023] However, when the X-ray diffraction pattern of some samples was compared, it turned out that the intensity ratio of each peak is not fixed by the sample, the orientation condition of the microcrystal in it differs also in the lithium foil of the same lot considerably, and the sample with quite low crystallinity also exists. Since this lithium foil extrudes this and it is manufactured by molding, it is considered that the direction of that microcrystal became in the scattering direction.

[0024] According to the JCPDS card (number 150401), with the X diffraction pattern of a lithium metal, as shown in drawing 6 , the following seven peaks are observed. That is, it is a peak equivalent to 110 reflection, 200 reflection, 211 reflection, 220 reflection, 310 reflection, 222 reflection, and 321 reflection. And those peak intensity ratios are 42.9%, 12.9%, 17.1%, 8.6%, 8.6%, 1.3%, and 8.6% at the order like the point. When this peak intensity ratio is considered to be a criterion and it has 50% or more of peak intensity ratio about the peak of other reflection 70% or more in the case of the peak of 110 reflection, it is possible that the crystal face equivalent to each peak is carrying out orientation of the microcrystal in a lithium foil to the field which irradiated the X-ray quite preferentially.

[0025] The charge and discharge of the cell using the lithium metal as a negative electrode are equivalent to the deposit lytic reaction of a lithium. When it thinks microscopically, the energy which the deposit dissolution of a lithium takes by the difference in the crystal face must be different, respectively. therefore, when the one crystal face is carrying out orientation to the front face of the lithium metal which is a substrate preferentially, distribution of the energy of the deposit dissolution of a lithium stops -- having -- in addition -- and it is thought that deposit lytic reaction advances to homogeneity.

[0026] However, the surface coat always forms in the front face of a lithium metal, advance of a surface coat and surface reaction which does not cause a reaction failure as much as possible can follow to the deposit and the dissolution of a lithium in the maximum front face, and a uniform reaction can be advanced continuously for the first time.

[0027] That is, the matter which has adjustment in the front face of a lithium sheet with a uniform crystal structure to the surface atomic arrangement of the lithium sheet serves as a surface coat, and it is desirable for a crystal structure to be uniform also inside a surface coat. When a charge-and-discharge cycle is piled up always maintaining such structure, uniform deposit lytic reaction will advance and a dendrite deposit will be controlled.

[0028] Here, the crystal face (100) of a lithium metal is considered, referring to drawing 1 . Since a lithium metal takes a body-centered cubic lattice, the crystal face (100) has the periodic structure of a grid where the lithium atom is located at each square top-most vertices. The lattice constant at that time is 3.51. When the square of the superlattice which makes the diagonal line of the square one side is considered to it, the die length applies the square root of 2, and is set to 4.96. Moreover, the square of this superlattice is the structure where 1 lithium atom is located at the core and the lithium atom exists in each top-most vertices further. This structure is of the same type as the array of the crystal face (100) of a face-centered cubic lattice, and it turns out that it is equivalent to the location of the alkali metal of the rock salt mold crystal structure.

[0029] That is, it turns out that it can change from an atom to ion and a surface coat can be formed now, without performing atomic big migration for a lithium atom by forming in the front face of the lithium sheet of crystal-face (100) orientation the surface coat of the rock salt mold crystal structure which consists of a lithium and a halogen.

[0030] Then, the negative electrode for nonaqueous electrolyte cells with which it is the sheet which uses a lithium metal as an active material as a gestalt of operation of this invention, and the crystal face in the body-centered cubic lattice crystal structure (100) has the surface coat structure where the surface coat which uses as a principal component the matter of the rock salt mold crystal structure currently formed with adjustment sufficient to the atomic arrangement of the front face was made to form in a lithium sheet with the uniform structure which is carrying out orientation with the priority to a sheet

front face is used. The matter with the structure in which the crystal face (100) is carrying out orientation preferentially to the sheet front face as a surface coat of the rock salt mold crystal matter at that time is desirable. Furthermore, the rock salt mold crystal matter has the desirable halogenide of a lithium.

[0031] Moreover, as a gestalt of other operations of this invention, in order to make LiCl form as crystal matter of a rock salt mold, it produces by dipping the lithium sheet in which the crystal face (100) is carrying out orientation with the priority to a sheet front face in the electrolytic solution containing a chlorine molecule or a chlorine ion. The approach of adding the organic solvent which blew chlorine gas to the electrolytic solution as an approach of making the electrolytic solution at that time containing a chlorine molecule or a chlorine ion is desirable. Moreover, as the chlorine gas entrainment organic solvent, it is desirable to use dimethoxyethane.

[0032] By the way, to the surface atomic structure, the misfit relaxation in which the matter which is different in grid relaxation while maintaining adjustment despite the lifting is formed is said to be possible, if the gap with a front face becomes to about 10%. That is, when it thinks from the value of 4.96 of the above-mentioned superlattice period, a lattice constant a is 4.46. <a<5.46 It is thought that the above conditions are attained by within the limits.

[0033] Furthermore, when misfit relaxation is less than 1%, almost epitaxial growth has taken place and it can be said that it is in the good condition which does not almost have distortion of a front face. The range of the lattice constant a at that time is 4.91. <a<5.01 It becomes. That is, it will be good if the surface coat in which it has the rock salt mold crystal structure, and a lattice constant has the value of the above-mentioned range is producible.

[0034] If it is the matter with the rock salt mold crystal structure and is the matter with a suitable lattice constant when it thinks only with the value of a lattice constant, a surface coat with sufficient adjustment will be formed. Furthermore, a situation will be more good if it has a lattice constant with such sufficient adjustment by the halogenide of a lithium. Here, the comparison with the above-mentioned lattice constant is considered by the halogenide of a lithium as rock salt mold crystal structure matter. For the lattice constant of LiCl, 5.14 and LiBr are [4.026 and LiI of 5.5013 and LiF] 6.0. LiF will become, and if it thinks on the basis of 4.96, in LiBr, LiI will become [a gap of LiCl] +21.0% -18.8% +10.9% +3.6%. That is, in the case of these simple substance matter, although LiCl is applied within 10%, LiBr, and LiF and LiI will not be applied.

[0035] Then, by the halogenide of a lithium, in order to bring close to the value of 4.96 of a superlattice period more, such combination must be considered. For example, since it exists between LiF and LiCl, if the VEGARD rule about a lattice constant is applied, by one sixth, LiF is set to a= 4.9543, when LiCl makes the solid solution of five sixths of allocation form, a misfit value is -0.1% and, as for this lattice constant 4.96, a coat with very high adjustment may be able to form it. However, as shown also in a phase diagram, in the usual thermal equilibrium-process, the solid solution of LiF-LiCl is unproducible. However, in the case of a reaction in the environment only near the front face in the condition that the location of a lithium was fixed considerably limited very much, the above-mentioned matter may be able to produce.

[0036] Limit the above-mentioned view and it is not necessarily applied only to the combination of LiF and LiCl. That is, if LiF shorter than 4.96 is included, the lattice constant to need can be obtained with at least one sort of combination among LiCl, LiBr, and LiI.

[0037] Then, in order that the solid solution of at least one sort and LiF may form the surface coat which is a principal component among LiCl, LiBr, and LiI as matter which adjusted the lattice constant with the crystal structure of a rock salt mold as a gestalt of other operations of this invention (100) The lithium sheet in which the crystal face is carrying out orientation with the priority to a sheet front face The manufacture approach of producing the negative electrode for nonaqueous electrolyte cells is used by dipping in the electrolytic solution which contains at least one sort, a fluorine molecule, or fluorine ion among a chlorine molecule or a chlorine ion, a bromine molecule or bromine ion, an iodine molecule, or iodine ion.

[0038] Hereafter, the example of this invention is explained to a detail, referring to a drawing. In

addition, all the following processings were performed in the argon gas ambient atmosphere.
[0039] (Example 1) As an active material ingredient, the lithium foil with 100 micrometers [in thickness] and a width of face of 22mm was used. After one side cut off this lithium foil in the shape of [which is 22mm] a square and folded it up to 1/16, it pressed for 10 seconds by the pressure of 250kg/cm2 using the steel fixture with the field by which mirror polishing was carried out. The obtained lithium foil was folded up again and it pressed by the same approach. Then, the activity which presses the lithium foil for 10 seconds by the pressure of 200kg/cm2 as it is, without folding up shortly was repeated twice. That is, a total of four press processings was given to the lithium foil. The thickness of a lithium foil was set to about 100 micrometers comparable as the beginning by doing this activity. Although the front face of the prepared lithium foil was carrying out blunt metallic luster, the lithium foil which performed this press processing compared with it had the metallic luster front face which shone very much.
[0040] About this lithium foil, X-ray analysis was performed using CuK alpha rays. The result was shown in drawing 2 . The obtained diffraction pattern had the very large reinforcement of the diffraction peak of 200 reflection, and the peak intensity of 200 reflection formed about 91% of the sum of the peak intensity of all the acquired diffraction peaks so that drawing 2 might show. The preferential stacking tendency of such a 200 reflective peak was observable over the lithium foil at large which performed the above-mentioned press processing.
[0041] In such a lithium foil, the front face of a lithium foil will carry out orientation very preferential to the crystal face (100). And since the front face is carrying out metallic luster with which it shone very much, it is thought that a surface coat is thin.
[0042] In order first to check that the coat of the rock salt mold crystal structure is producible on the front face of this lithium foil, the following electrolytic solutions were produced and it decided to dip a crystal-face (100) orientation lithium foil into it.
[0043] In order to make a LiCl coat produce, it decided to use as the electrolytic solution what was usually added to the electrolytic solution using the organic solvent which blew chlorine gas. First, chlorine gas was blown into 100ml dimethoxyethane for 1 minute by flow rate 10 cc/min, and the chlorine gas entrainment organic solvent was produced. And this chlorine gas entrainment dimethoxyethane was added at a rate of 5 ml/L in the solution dissolved in the mixed solvent of ethylene carbonate and diethyl carbonate (volume ratio 1:1) at a rate that LiClO4 is one mol/l.
[0044] Into this electrolytic solution, after dipping a previous crystal-face (100) orientation lithium foil for three days, in order to investigate the structure of that front face, CuK alpha rays were used and X-ray analysis was performed. The result was shown in drawing 3 . It turns out that it exists while the diffraction peak of 2theta's 200 reflection of the very big lithium at nearly 52 degrees is observed and the diffraction peak of nearly 36 110 reflection of 2theta becomes broadcloth for a while so that drawing 3 may show. These peaks exist in the same location as drawing 2 .
[0045] However, the peak which did not exist in drawing 2 was observed in the place whose 2theta is nearly 35 degrees, and it turned out that this is equivalent to the diffraction peak of 200 reflection of LiCl according to the JCPDS card (number 40664). Visually, the front face of the lithium metal at this time was in the situation that the gloss degree on the front face of a lithium at the time of press hardly changes. That is, it is thought that the thickness of the surface coat itself is very thin. In spite of it, it is thought that the preferential stacking tendency to the crystal face in the rock salt mold crystal structure (100) of the surface coat itself of the diffraction peak of 200 reflection having been checked is high. That is, by dipping the crystal-face (100) orientation lithium foil of a body-centered cubic lattice crystal structure into the electrolytic solution which added the chlorine content organic solvent showed that the surface lining of LiCl which carried out orientation with the priority to the crystal face (100) of a rock salt mold crystal structure was formed in the front face.
[0046] Then, the flat nonaqueous electrolyte rechargeable battery which indicates the dimethoxyethane which blew chlorine gas to be a crystal-face (100) orientation lithium foil at drawing 4 using the electrolytic solution added at a rate of 5 ml/L to the mixed solvent of one-mol [/l.] LiClO4 (ethylene carbonate, diethyl carbonate 1) was produced. A production procedure is explained referring to drawing

4 .

[0047] The positive-electrode charge collector 2 which used the expanded metal made from titanium into the positive-electrode can 1 has been arranged, and spot welding of both was carried out. the positive electrode which mixed $LiCoO_2$ powder, carbon black, and polytetrafluoro ethylene powder -- above the positive-electrode charge collector 2, specified quantity restoration was carried out, the mixture was pressurized, and the positive electrode 3 was formed.

[0048] The negative electrode 6 which becomes the obturation plate 5 which carried out spot welding of the negative-electrode charge collector 4 using the expanded metal made from nickel beforehand from the lithium foil of the shape of a disk which performed the above-mentioned press processing was stuck by pressure.

[0049] After having arranged the separator 7 which consists of a porosity film made from polypropylene above a positive electrode 3, the electrolytic solution was poured in into the positive-electrode can 1, the obturation plate 5 was further fitted in through the gasket 8 at opening of the positive-electrode can 1, and the flat nonaqueous electrolyte rechargeable battery was assembled to it.

[0050] Moreover, the same nonaqueous electrolyte rechargeable battery was assembled, using the lithium foil which has processed nothing as a negative electrode, received as an example of a comparison. It produced such ten cells at a time in the example and the example of a comparison, respectively.

[0051] Under the 20-degree C environment, with the current density of 2 mA/cm2, the charge-and-discharge cycle trial which sets 2.0V and a charge upper limit electrical potential difference to 3.5V for a discharge minimum electrical potential difference was performed, and the cycle life was searched for about these cells. However, the cycle life was made into the life in the cycle, when it considered as a life in the place where discharge capacity became half [of 1 cycle eye] and the internal short circuit by the dendrite occurred in the middle of a charge-and-discharge cycle.

[0052] The result is shown in Table 1. The value of the cycle life of front Naka shows average **sigma.

[0053]

[Table 1]

	サイクル寿命
実施例１	２１６±１２
比較例１	１２７±２５

[0054] From Table 1, a ******** understands a charge-and-discharge cycle life for the cell of the example 1 which used the electrolytic solution which added the chlorine gas entrainment organic solvent further compared with the example 1 of a comparison using a crystal-face (100) orientation lithium. Moreover, as for the cell of an example 1, the variation is also known by decreasing compared with the cell of the example 1 of a comparison.

[0055] This is considered to be the result of the electrochemical dissolution of a lithium and the reaction of a deposit advancing smoothly, and a dendrite deposit, isolation by cutting of the lithium at the time of the dissolution, etc. decreasing, and performing a charge-and-discharge cycle very efficiently, since the halogenide (in this case, LiCl) of a lithium with a rock salt mold crystal structure is formed with sufficient adjustment as a surface coat of a crystal-face (100) orientation lithium. Moreover, it turns out that variation is also reduced with improvement in a cycle life, and precision is also high.

[0056] Therefore, by constructing a cell using the lithium sheet which is carrying out preferential orientation to the crystal face (100), and the electrolytic solution which added the chlorine gas entrainment organic solvent, and performing charge and discharge using the negative electrode which produced the LiCl surface coat on the front face of a lithium foil shows that a charge-and-discharge

cycle life becomes long, and precision's improves.
[0057] In addition, in this example, although LiCl was used as rock salt mold crystal matter of a surface coat, even if it formed the surface coat of LiF, LiBr, and LiI by the same technique, the same effectiveness was able to be acquired.
[0058] (Example 2) As an active material ingredient, the lithium foil with 100 micrometers [in the same thickness as an example 1] and a width of face of 22mm was used. And the same press processing as an example 1 was performed to this lithium foil. By this press processing, the preferential stacking tendency of the crystal face (100) of a lithium was seen like the example 1.
[0059] Then, in order to check that the coat of the solid solution of LiF and LiCl which has the rock salt mold crystal structure in the front face of this lithium foil first can double and produce a lattice constant like an example 1, the following electrolytic solutions were produced and it decided to dip a crystal-face (100) orientation lithium foil into it.
[0060] What dissolved LiPF6 and LiClO4 by the concentration of one mol/l. into the mixed solvent of ethylene carbonate and diethyl carbonate (volume ratio 1:1) by the ratio of 1:30 was used as the electrolytic solution. In this case, a fluorine atomic number: The ratio of a chlorine atomic number is set to 1:5. Into this electrolytic solution, after dipping a previous crystal-face (100) orientation lithium foil for three days, CuK alpha rays were used for the structure of that front face, and X-ray analysis was performed. The result was shown in drawing 5 .
[0061] While the diffraction peak of 2theta's 200 reflection of the very big lithium at nearly 52 degrees is observed and the diffraction peak of nearly 36 110 reflection of 2theta becomes broadcloth so that drawing 5 may show, it turns out that it exists as a small peak. These peaks exist in the same location as drawing 2 . However, although the peak which existed in the angle-of-elevation side very near the peak of 110 reflection neither by drawing 2 nor drawing 3 was observed and this was not able to be checked with a JCPDS card, it is guessed by the count shown below that it is the crystal face (100) of the solid solution of LiF and LiCl.
[0062] According to the JCPDS card (number 40857) of LiF, and the JCPDS card (number 40664) of LiCl, as for the peak (200) of LiF, 2theta exists [d value] in 44.99 degrees by 2.013, and, as for the peak (200) of LiCl, it turns out that 2theta exists [d value] in 34.88 degrees by 2.57. If LiF follows a VEGARD rule when LiCl dissolves by one sixth and LiF and LiCl dissolve at five sixths of a rate, a lattice constant will be set to 4.9543 (200) and d value will become 2.477 of one half in the crystal face. In this d value, when it calculates on the wavelength 1.5405 of CuK alpha rays, the peak of the 200 reflection of the solid solution of LiCl and LiF to the place whose 2theta is 36.23 degrees will appear. Moreover, visually, most gloss degrees on the front face of a lithium at the time of press were in the situation not changing like [the front face of the lithium metal at this time] the case of an example 1. That is, like the case of an example 1, a surface coat is very thin and it is thought that the preferential stacking tendency to the crystal face (100) is high.
[0063] That is, it turned out that LiF and LiCl form the solid solution and the surface coat the crystal face (100) of the rock salt mold crystal structure is carrying out [the coat] orientation preferentially is formed. Although the crystal structure in this case is not analyzed in a detail, a lithium ion exists in the location of the face centered cubic of a rock salt mold crystal structure, one of the halogens which enclose the surroundings of it by 6 coordination is F ion, and it is thought that the structure from which five became Cl ion is taken. When small F ion exists equally by one sixth in big Cl ionic radius, a lattice constant becomes small on the average, and it is thought that the value according to a VEGARD rule is shown. Usually, as shown also in a phase diagram, in a thermal equilibrium-process, the solid solution is unproducible, but it is only near the front face, and since it is in the situation limited very much of being dependent on the condition of the crystal face of a substrate, it is thought that the solid solution of such LiF and LiCl was producible.
[0064] Then, the flat nonaqueous electrolyte rechargeable battery which shows a crystal-face (100) orientation lithium foil and the mixed salt of (LiPF6:LiClO4=1:30) to drawing 4 like an example 1 using the mixed solvent of the ethylene carbonate included at a rate of one mol/l. and diethyl carbonate (volume ratio 1:1) was produced.

[0065] Moreover, the same nonaqueous electrolyte rechargeable battery was assembled, using the lithium foil which has processed nothing as a negative electrode, received as an example of a comparison. Thus, the cell of an example and ten cells of the example of a comparison were produced, respectively, and the same charge and discharge test as an example 1 was performed.
[0066] The result is shown in Table 2. The value of the cycle life of front Naka shows average **sigma.
[0067]
[Table 2]

	サイクル寿命
実施例２	２５０±１２
比較例２	１０５±２３

[0068] Using a crystal-face (100) orientation lithium, the cell of the example 2 which used the electrolytic solution containing the mixed salt which sets the mixing ratio of two sorts of salts, LiPF6 and LiClO4, to 1:30 further at the aforementioned order has a long charge-and-discharge cycle life compared with the example 2 of a comparison, and Table 2 shows that the variation is also reduced.
[0069] The halogenide (in this case, solid solution of LiF and LiCl) of a lithium with a rock salt mold crystal structure this (100) Since the lattice constant has the structure formed in the condition that adjustment is high, very much of being almost the same, as a surface coat of a crystal-face orientation lithium The electrochemical dissolution of a lithium and the reaction of a deposit advance smoothly, a dendrite deposit, isolation by cutting of the lithium at the time of the dissolution, etc. decrease, and it is thought that it is the result of performing a charge-and-discharge cycle very efficiently. Moreover, it turns out that variation is also reduced with improvement in a cycle life, and precision is also high.
[0070] Moreover, compared with the cell of an example 1, as for the cell of an example 2, it turns out that the life is long further. By using the surface coat which does not almost have a gap of a lattice constant, the reaction of the deposit dissolution advances to homogeneity further, the depressor effect of a dendrite deposit is demonstrated, and this is considered to be because for improvement in charge-and-discharge effectiveness to have been obtained.
[0071] Therefore, by constructing a cell using the electrolytic solution which added the chlorine gas entrainment organic solvent, and performing charge and discharge using the negative electrode which produced the LiCl surface coat on the front face of a lithium foil shows that a charge-and-discharge cycle life becomes long, and precision's improves.
[0072] Therefore, by constructing a cell using the electrolytic solution containing the lithium sheet which is carrying out preferential orientation to the crystal face (100), and the mixed salt of two sorts of salts, LiPF6 and LiClO4, and performing charge and discharge using the negative electrode which produced the surface coat of the solid solution of LiF and LiCl on the surface of the lithium shows that a charge-and-discharge cycle life becomes long, and precision's improves.
[0073] In addition, in this examples 1 and 2, although LiCoO2 was used as a positive electrode, the stratified oxide of LiNiO2 and LiMnO2 grade, the spinel mold oxide of LiMn2O4 grade, V system oxide of V2O5 grade, and an ingredient called TiS2 may be used as other positive electrodes.
[0074]
[Effect of the Invention] As mentioned above, according to this invention, it became possible to perform the charge and discharge of uniform deposit lytic reaction, i.e., a cell, by forming the surface coat structure which uses as a principal component the matter to which the crystal face (100) has the rock salt mold crystal structure in the front face of the lithium sheet which is carrying out orientation preferentially with the sheet which uses a lithium metal as an active material. Furthermore, the dendrite deposit reaction of the lithium metal which is an active material was able to be suppressed, and

effectiveness, such as improvement in the cycle life of a cell and improvement in precision, was able to be acquired.

[Translation done.]